



Graft copolymers from cellulose: Synthesis, characterization and evaluation



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ABSTRACT

Cellulose, a linear polysaccharide polymer with numerous glucose monosaccharide units is of enormous interest because of its applications in biosorption, biomedical, packaging, biofiltration and biocomposites. In this study, cellulose-graft-poly(butyl acrylate) copolymers were synthesized under microwave conditions. Effects of microwave radiation doses and different reaction parameters were optimized to get the optimum percentage of grafting. The dependence of optimum conditions for better physico-chemical properties of the cellulosic polymers was also determined. Fourier transform infrared spectroscopy (FT-IR) analysis was used to authenticate the chemical reaction taking place between cellulosic polymers and monomer. The thermogravimetric behavior of the raw and grafted cellulosic polymers was characterized by thermogravimetric analysis (TGA). The surface structure of the raw and grafted cellulosic polymers was analyzed through scanning electron microscopy (SEM). The graft copolymers have been found to be more moisture resistant and also showed better chemical and thermal resistance.

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1. Introduction

The economy of depleting petroleum resources coupled with increasing environmental have ignited the interest in the use of renewable cellulosic polymers from different resources for making new materials (Nazi, Malek, & Kotek, 2012; Qiu, Ren, & Hu, 2012). Natural cellulosic polymers such as lignocellulosic natural fibers offer well-known advantages as compared to the traditional synthetic materials which include eco-friendliness, toxicologically harmless, biodegradability, carbon dioxide (CO₂) neutral, easy availability, enhanced energy recovery, non corrosive nature and usually lower cost (Singha & Thakur, 2010a). These cellulosic natural polymers are also characterized by a huge degree of variability and diversity in their properties depending upon the place of their origin (Thakur & Singha, 2011a). During the last few years a great deal of interest has been dedicated to the natural cellulosic polymers based materials as the unique properties exhibited by natural polymers are never offered by non cellulosic polymers. Naturally derived cellulosic polymers are usually eco-friendly, and therefore materials prepared using these polymers such as composites reinforced with natural fibers should also be eco-friendly (Liu, Wu, &

Zhang, 2009; Singha & Thakur, 2010a). Polymer composite materials containing cellulosic polymers exhibit enhanced properties and are less expensive than the starting polymer in overall material costs (Singha & Thakur, 2010b; Thakur & Singha, 2011b). Novel green materials based upon natural cellulosic polymers have been the subject of intense international research since last two decades and a number of practical applications are now emerging in various fields, including packaging, biomedical, bioenergy, bioplastics, and in aerospace industry (Akar, Altinisik, & Seki, 2012; Alila, Ferraria, do Rego, & Boufi, 2009; Bao, Ma, & Sun, 2012). Commercial interest in manufacturing different products using cellulosic polymers is driven by the derivation of these polymers from environmental friendly renewable sources as well as by their specific properties including biodegradability (Cheema, El-Shafei, & Hauser, 2013; Wu, 2012). However the natural cellulosic polymers are inferior to harsh environmental conditions due to hydrophilic nature of the cellulose and need to be modified for superior applications (Thakur, Singha, & Thakur, 2012a).

Among various natural cellulosic polymers, only few studies have been reported on the *cellulosic pine needles* based materials (Singha & Thakur, 2009; Thakur & Singha, 2011a). These needles are obtained from *Pinus* which is one of the most popular trees in almost all around the globe and is a rich source of cellulose in the form of *pine needles*. These needles are automatically shed off by the trees during whole year especially in summer and are one of the major reasons for destruction of different kinds of flora and fauna. In order to increase the physico-chemical properties of

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these needles for different potential applications we are working in the modification of the properties of these cellulosic polymers by graft copolymerization. Various modification techniques have been reported to improve the physico-chemical properties of natural polymers (Eissa, Khosravi, & Cimecioglu, 2012; Zhong, Chai, & Fu, 2012), and among these graft copolymerization have received much more attention during the last few decades (Abdel-Halim, 2012a; Mwaikambo & Ansell, 2002; Sand, Yadav, & Behari, 2010). It is one of the most facile methods to incorporate desired functional groups on to natural polymers depending upon the targeted application (Abdel-Halim, 2012b; Abdel-Halim & Al-Deyab, 2012; Oza, Meena, & Siddhanta, 2012; Unlu, Oztekin, & Atici, 2012). Surface modification of cellulosic polymers by graft copolymerization of vinyl monomer increases their functional properties, thus making them suitable for a number of applications (Ofomaja, Ngema, & Naidoo, 2012; Teli & Sheikh, 2012; Thakur, Singha, & Thakur, 2012b, 2012c). Our most recent work has explored the possibility of modifying the surface properties of a number of cellulosic polymers and their possible use as potential reinforcement in green composites (Thakur et al., 2012b). As a continuation, the present work describes an investigation of the effect of microwave radiation on the graft copolymerization of butyl acrylate onto *cellulosic pine needles*.

2. Experimental

2.1. Materials

Cellulosic pine needles were collected from local resources of Himalayan region. Reagent grade chemicals namely, butyl acrylate (BA), ferrous ammonium sulphate (FAS), potassium persulphate (KPS), sodium hydroxide (NaOH) and tetrahydrofuran were kindly supplied by Qualigens Chemicals Ltd. Company. Purification of *cellulosic pine needles*, grafting reactions, and separation of homopolymer from the grafted *cellulosic pine needles* were carried out according to the standard procedure reported in literature (Singha & Thakur, 2009; Thakur, Singha, & Misra, 2011). The chemicals used were purified where necessary.

2.2. Graft copolymerization onto *cellulosic pine needles*

Prior to graft copolymerization synthesis, chemical modification of the *cellulosic pine needles* was done through mercerization of these cellulosic needles as per standard method reported in our earlier studies (Singha & Thakur, 2009; Thakur et al., 2012a). Graft copolymerization synthesis was carried out by immersing mercerized *cellulosic pine needles* in a specific amount of distilled water for 24 h followed by addition of known amount of initiator (FAS–KPS) with continuing stirring for 5–10 min in order to create sufficient free radical sites on the surface of the cellulosic fibers. Then to start the copolymerization, monomer (BA) was added into the reaction flask containing the mercerized cellulosic biofibers in the microwave oven. The reaction mixture was stirred at selected doses for different time intervals to optimize different conditions of solvent, time, initiator and monomer concentration for maximum percentage of grafting (Kamel, 2012; Mishra, Rani, & Sen, 2012; Thakur & Singha, 2011b). After the completion of the reaction, the sample was filtered, washed with distilled water several times and then air-dried. The dried *cellulosic pine needles* were extracted with tetrahydrofuran in a Soxhlet extraction apparatus for 50 h to remove the homo-polymer formed during graft copolymerization. After extraction, the samples were washed with distilled water to remove impurities. The graft copolymers freed from homopolymer was then dried in a hot air oven to a constant weight.

2.3. Determination of percentage of grafting

The percentage grafting (P_g) was calculated as per the standard method in the following manner (Thakur et al., 2012a):

$$\text{Percent grafting } (P_g) = \frac{W_g - W}{W} \times 100$$

where W is the weight of raw cellulosic polymer, W_g is the weight of grafted cellulosic polymer. Characterization of poly(BA)-g-cellulosic pine needles

2.3.1. Infra red spectroscopy (IR)

The changes in the chemical structure of the *cellulosic pine needles* as a result of graft copolymerisation synthesis with BA monomer was characterized using Fourier transform infra red spectroscopy (FTIR) with the help of KBr pellets on Perkin Elmer RXI Spectrophotometer in order to confirm the synthesis of graft copolymers *cellulosic pine needles*-g-poly-(BA). The spectrum was recorded in the range of 400–4000 cm^{-1} .

2.3.2. Scanning electron microscopy (SEM)

The surface morphology of raw and grafted *cellulosic pine needles* was observed by using scanning electron microscopy machine (LEO 435 VP). All the samples were gold coated before observation.

2.3.3. Thermal analysis

Thermo gravimetric analyses (TGA) of the raw and grafted *cellulosic pine needles* were carried out in nitrogen atmosphere on a thermal analyzer (Perkin Elmer) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The sample weights of raw and grafted *cellulosic pine needles* for TGA studies were 10 mg each.

2.4. Physico-chemical characterization of raw and grafted *cellulosic pine needles*

2.4.1. Swelling behavior

Swelling studies of the raw and grafted *cellulosic pine needles* were carried out as per standard method in different solvents such as dimethyl formamide, water, methanol and isobutyl alcohol. The percent swelling was calculated from the increase in initial weight in the following manner (Thakur et al., 2012a):

$$\text{Percent swelling } (P_s) = \frac{W_f - W_i}{W_i} \times 100$$

2.4.2. Moisture absorbance behavior

The study of the moisture absorbance behavior of the raw and grafted *cellulosic pine needles* was made in a humidity chamber. Known weights of dry grafted and raw *cellulosic pine needles* were placed in the humidity chamber for particular time interval under different humidity levels ranging from 20% to 90%. Final weights of the samples exposed to different humidity levels were then noted. The percent moisture absorbance ($\%M_{\text{abs}}$) was calculated from the increase in initial weight in the following manner (Thakur et al., 2012a):

$$\% \text{ Moisture absorbance } (\%M_{\text{abs}}) = \frac{W_f - W_i}{W_i} \times 100$$

where W_f is the weight of grafted *cellulosic pine needles*; W_i is the weight of raw *cellulosic pine needles*. Chemical resistance behavior

The chemical resistance behavior of the raw and grafted *cellulosic pine needles* was studied in acid and base environments. Acid and base resistance was found out by placing a known weight (T_w) of *cellulosic pine needles* in fixed volume of 1 N HCl and 1 N NaOH and the weight of the samples were noted down after certain intervals. The chemical resistance of grafted as well as ungrafted *cellulosic*

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